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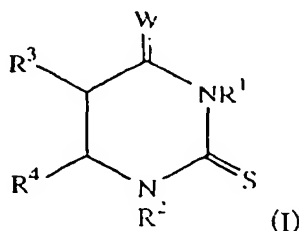
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(54) **Cyclic thioureas as additives for lubricating oils**

(57) A composition comprising (a) from 0.1% to 20% of at least one cyclic thiourea compound of formula I:



wherein W is O or S; R<sup>1</sup> and R<sup>2</sup> independently are hydrogen, alkyl, alkenyl, aryl or aralkyl; R<sup>3</sup> and R<sup>4</sup> independently are hydrogen, alkyl, alkenyl, aryl or aralkyl, or R<sup>3</sup> and R<sup>4</sup> groups combine with ring carbon atoms to which they are attached to form a five- to seven-membered heterocyclic ring; and (b) a lubricating oil.

**Description**Background

[0001] This invention relates generally to cyclic thioureas useful as additives for lubricating oils.

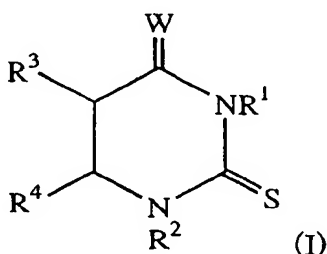
[0002] Zinc dialkyldithiophosphates (ZDDP) are widely used as lubricant additives. The principal disadvantages of these compounds are that an ash residue is produced by the zinc as the additive is consumed, and that phosphorus is known to affect the efficiency of catalytic converters in motor vehicles, thereby causing emissions problems. Cyclic thiourea compounds useful as lubricant additives are disclosed in U.S. Patent No. 5,935,913. However, the compounds disclosed therein are not within the scope of the present invention.

[0003] The problem addressed by this invention is to find additional non-metallic, non-phosphorus-containing oil-soluble additives for lubricating oils.

Statement of Invention

[0004] The present invention is directed to a composition comprising:

(a) from 0.1% to 20% of at least one cyclic thiourea compound of formula I:



wherein W is O or S; R<sup>1</sup> and R<sup>2</sup> independently are hydrogen, alkyl, alkenyl, aryl or aralkyl; R<sup>3</sup> and R<sup>4</sup> independently are hydrogen, alkyl, alkenyl, aryl or aralkyl, or R<sup>3</sup> and R<sup>4</sup> groups combine with ring carbon atoms to which they are attached to form a five- to seven-membered heterocyclic ring; and

(b) a lubricating oil.

[0005] The present invention is further directed to a method for improving the anti-wear characteristics of a lubricating oil by adding from 0.1% to 20% of a compound of formula I.

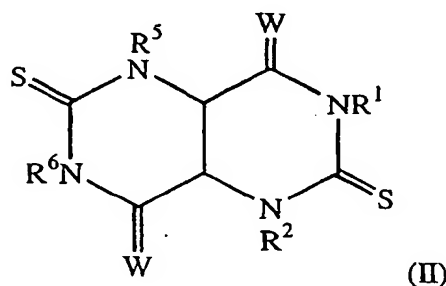
Detailed Description

[0006] All percentages are weight percentages based on the entire composition described, unless specified otherwise. An "alkyl" group is a saturated hydrocarbyl group having from one to twenty-two carbon atoms in a linear, branched or cyclic arrangement, and having from 0 to 2 oxygen, nitrogen or sulfur atoms. Substitution on alkyl groups of one or more halo, hydroxy, alkoxy, alkanoyl or amido groups is permitted; alkoxy, alkanoyl and amido groups may in turn be substituted by one or more halo substituents. In one preferred embodiment, alkyl groups contain from one to twelve carbon atoms and from 0 to 1 oxygen, nitrogen or sulfur atoms; in another preferred embodiment, alkyl groups contain from 12 to 22 carbon atoms, and more preferably, no heteroatoms. An "alkenyl" group is an "alkyl" group in which at least one single bond has been replaced with a double bond. An "aryl" group is a substituent derived from an aromatic compound, including heterocyclic aromatic compounds having heteroatoms chosen from among nitrogen, oxygen and sulfur. An aryl group has a total of from five to twenty ring atoms, and has one or more rings which are separate or fused. Substitution on aryl groups of one or more halo, alkyl, alkenyl, hydroxy, alkoxy, alkanoyl or amido groups is permitted, with substitution by one or more halo groups being possible on alkyl, alkenyl, alkoxy, alkanoyl or amido groups. An "aralkyl" group is an "alkyl" group substituted by an "aryl" group. A "lubricating oil" is a natural or synthetic oil, or a mixture thereof, having suitable viscosity for use as a lubricant, e.g., as crankcase oil in an internal combustion engine, automatic transmission fluid, turbine lubricant, gear lubricant, compressor lubricant, metal-working lubricant, hydraulic fluid, etc.

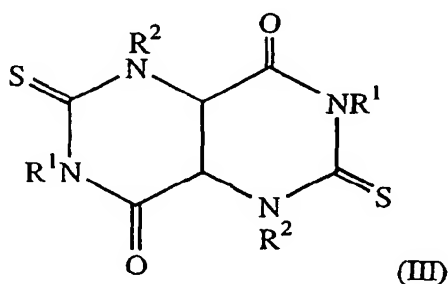
[0007] In one embodiment of the invention, preferably formula (I) has R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> which independently are hydrogen, alkyl, alkenyl, aryl or aralkyl, i.e., the compound is not bicyclic. Preferably, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> independently

are hydrogen, alkyl or alkenyl, more preferably at least one of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is  $C_6$ - $C_{22}$  alkyl or alkenyl, more preferably at least one of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is  $C_{10}$ - $C_{22}$  alkyl, and most preferably at least one of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is  $C_{16}$ - $C_{22}$  alkyl.

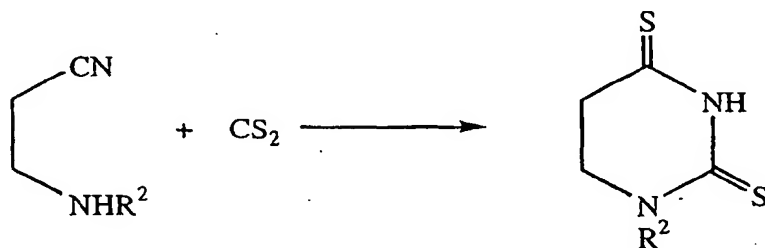
[0008] In another embodiment of the invention  $R^3$  and  $R^4$  groups in formula I combine with ring carbon atoms to which they are attached to form a five- to seven-membered heterocyclic ring. In a preferred embodiment  $R^3$  and  $R^4$  groups combine to form the following bicyclic system of formula (II):



wherein  $R^5$  and  $R^6$  independently are hydrogen, alkyl, alkenyl, aryl or aralkyl. In a preferred embodiment of the invention, in which W is O,  $R^1$  and  $R^6$  are the same, and  $R^2$  and  $R^5$  are the same, the compound is a symmetric bicyclic compound of formula (III):

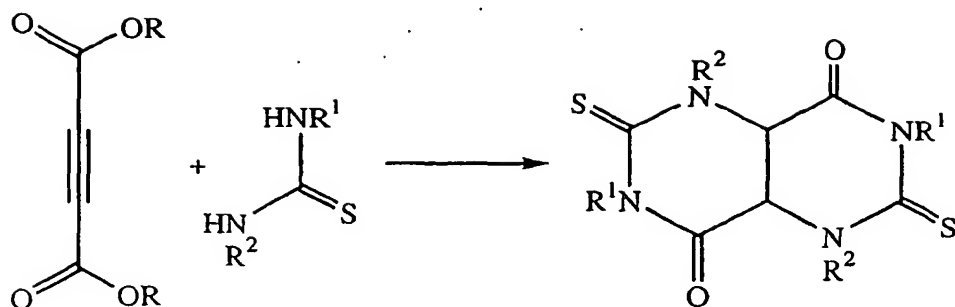


[0009] In one embodiment of the invention, a compound of formula (I) is prepared from a 2-amino alkyl nitrile and carbon disulfide, as shown below:



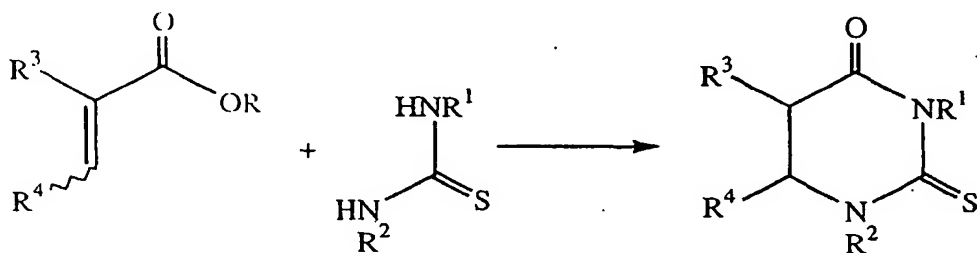
Preferably,  $R^2$  is  $C_6$ - $C_{22}$  alkyl or alkenyl, more preferably  $C_{10}$ - $C_{22}$  alkyl, and most preferably  $C_{16}$ - $C_{22}$  alkyl. Preferably,  $R^2$  is derived from an unsubstituted  $C_{16}$ - $C_{22}$  alkyl amine,  $R^2NH_2$ , preferably one which is an oil-soluble amine. In one preferred embodiment, the alkyl amine is a tertiary alkyl primary amine, i.e., a primary amine in which the alkyl group is attached to the amino group through a tertiary carbon. Examples of commercially available tertiary alkyl primary amines are the Primene<sup>TM</sup> amines available from Rohm and Haas Company, Philadelphia, PA.

[0010] In one embodiment of the invention, a compound of formula (III) is prepared from a substituted thiourea and a di-ester of acetylenedicarboxylic acid, as shown below:



The R groups are alkyl, alkenyl, or aralkyl groups, preferably C<sub>1</sub>-C<sub>4</sub> alkyl groups. Preferably, R<sup>1</sup> and R<sup>2</sup> are hydrogen, alkyl or alkenyl, more preferably at least one of R<sup>1</sup> and R<sup>2</sup> is C<sub>6</sub>-C<sub>22</sub> alkyl or alkenyl, more preferably at least one of R<sup>1</sup> and R<sup>2</sup> is C<sub>10</sub>-C<sub>22</sub> alkyl and most preferably at least one of R<sup>1</sup> and R<sup>2</sup> is C<sub>16</sub>-C<sub>22</sub> alkyl.

[0011] In one embodiment of the invention, a compound of formula (I) is prepared from a substituted thiourea and an ester of a  $\alpha,\beta$ -unsaturated carboxylic acid, as shown below:



Preferably, R<sup>3</sup> and R<sup>4</sup> are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl. Preferably, R<sup>1</sup> and R<sup>2</sup> are hydrogen, alkyl or alkenyl, more preferably at least one of R<sup>1</sup> and R<sup>2</sup> is C<sub>6</sub>-C<sub>22</sub> alkyl or alkenyl, more preferably at least one of R<sup>1</sup> and R<sup>2</sup> is C<sub>10</sub>-C<sub>22</sub> alkyl, and most preferably at least one of R<sup>1</sup> and R<sup>2</sup> is C<sub>16</sub>-C<sub>22</sub> alkyl.

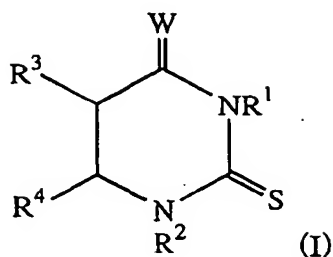
[0012] Preferably, the compound(s) of formula (I) is present in a lubricating oil in a total amount of at least 0.2%, more preferably at least 0.3%, and most preferably at least 0.4%. Preferably, the compound(s) of formula (I) is present in a lubricating oil in a total amount no greater than 10%, more preferably no greater than 5%, and most preferably no greater than 2%. Preferably, the compounds are soluble at the aforementioned levels.

[0013] Optionally, other additives typically used in lubricating oils are present in the composition. Such additives include, but are not limited to other anti-wear additives, anti-corrosion additives, dispersants, detergents, antioxidants, antifoamants, friction modifiers, seal swell agents, demulsifiers, viscosity index improvers and pour point depressants. Other anti-wear additives that can be used in combination with the compound of formula (I) include the commercial products known as ZDDP which are zinc dialkyldithiophosphates. In addition to improving the anti-wear characteristics of lubricating oils, the compound of formula (I) typically also improves anti-corrosion characteristics and functions as an anti-oxidant.

## Claims

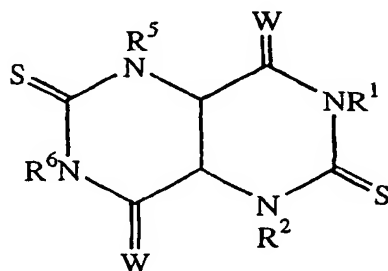
1. A composition comprising:

(a) from 0.1% to 20% of at least one cyclic thiourea compound of formula I:



wherein W is O or S; R<sup>1</sup> and R<sup>2</sup> independently are hydrogen, alkyl, alkenyl, aryl or aralkyl; R<sup>3</sup> and R<sup>4</sup> independently are hydrogen, alkyl, alkenyl, aryl or aralkyl, or R<sup>3</sup> and R<sup>4</sup> groups combine with ring carbon atoms to which they are attached to form a five- to seven-membered heterocyclic ring; and  
(b) a lubricating oil.

2. The composition of claim 1 in which W is O, and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> independently are hydrogen, alkyl, alkenyl, aryl or aralkyl.
3. The composition of claim 2 in which R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> independently are hydrogen or alkyl.
4. The composition of claim 3 in which at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is C<sub>6</sub>-C<sub>22</sub> alkyl.
5. The composition of claim 1 in which W is S, and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> independently are hydrogen, alkyl, alkenyl, aryl or aralkyl.
6. The composition of claim 1 in which R<sup>3</sup> and R<sup>4</sup> groups combine with ring carbon atoms to which they are attached to form a five- to seven-membered heterocyclic ring.
7. The composition of claim 6 in which the cyclic thiourea has formula



wherein R<sup>5</sup> and R<sup>6</sup> independently are hydrogen, alkyl, alkenyl, aryl or aralkyl.

8. The composition of claim 7 in which W is O, R<sup>1</sup> and R<sup>6</sup> are the same, and R<sup>2</sup> and R<sup>5</sup> are the same.
9. The composition of claim 8 in which R<sup>1</sup> and R<sup>2</sup> independently are hydrogen or alkyl.
10. The composition of claim 9 in which at least one of R<sup>1</sup> and R<sup>2</sup> is C<sub>6</sub>-C<sub>22</sub> alkyl.



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## EUROPEAN SEARCH REPORT

Application Number  
EP 03 25 4689

| DOCUMENTS CONSIDERED TO BE RELEVANT  |   |  |  |
|--|---|--|--|
| Category   | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim                                    | CLASSIFICATION OF THE APPLICATION (Int.Cl.7) |
| X  | US 3 939 084 A (SULLIVAN JAMES D)<br>17 February 1976 (1976-02-17)            | 1,6  | C10M135/16                                   |
| Y  | * column 15; table II *   | 1-10   |  |
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|  | * claim 1 *   |  |  |
|  | -----   |  |  |
|  |   |  | TECHNICAL FIELDS SEARCHED (Int.Cl.7)         |
|  |   |  | C10M<br>C07D                                 |
| The present search report has been drawn up for all claims   |   |  |  |
| Place of search<br>MUNICH  |   | Date of completion of the search<br>20 November 2003 | Examiner<br>Steendijk, M                     |
| <p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone<br/> Y : particularly relevant if combined with another document of the same category<br/> A : technological background<br/> O : non-written disclosure<br/> P : intermediate document</p> <p>T : theory or principle underlying the invention<br/> E : earlier patent document, but published on, or after the filing date<br/> D : document cited in the application<br/> L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p> |   |  |  |

EPO FORM 1503 (3.82) (P04001)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
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EP 03 25 4689

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20-11-2003

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